Supplementary Information for

Cobalt metalized polymer modulates the electronic structure of Pt

nanoparticles to accelerate water dissociation kinetics

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Materials:

Carbon nanotubes with carboxyl groups (CNT-COOH) were purchased from Beijing Deke Island Gold Technology Co., Ltd. 2,2-Dimethyl-1,3-propanediamine was purchased from Shanghai Haohong Biomedical Technology Co., Ltd. 4,4'-Dihydroxy-3,3'-diformylbiphenyl was obtained from Shanghai Haohong Biomedical Technology Co., Ltd. Melamine, phosphoric acid and $Co(NO_3)_2 \cdot 6H_2O$ were purchased from Aladdin Industrial Corporation (Shanghai, China). Dimethyl sulfoxide and absolute ethanol were purchased from Beijing Deke Island Gold Technology Co., Ltd. All reagents and solvents were used without further purification.

Synthesis of N P doped carbon nanotubes (NPCNs)

NPCNs was synthesized according to the procedure in the literature. CNT-COOH (100 mg) were added into a beaker containing 200 mL of ultrapure water and uniformly dispersed under ultrasound at room temperature for 4 h. Then transfer the uniformly dispersed CNT-COOH into a round bottom flask, melamine (250 mg) and phosphoric acid (0.32 mL) were added under strong stirring and react at 80 °C for 4 h. After cooling to room temperature, wash it with water and methanol for several times in turn, and finally put it into 60 °C vacuum drying oven for drying overnight. Finally, the resultant complex is pyrolyzed in N₂ atmosphere at 900 °C for 2 h with a ramp rate of 4 °C min⁻¹, affording the NPCNs assemblies as black powders.

Synthesis of (DMSO)Pt(Cl)₂

 K_2 [PtCl₄] (0.208 g, 0.5 mmol) was dissolved in water (2.5 mL), then dimethyl sulfoxide (DMSO, 92 µL, 1.5 mmol) was added and stirred at room temperature for 4 h. Centrifuge the reactants, wash the precipitates with water and ethanol, and finally vacuum drying at 40 °C overnight to afford the [(DMSO)Pt(Cl)₂] (182 mg, 0.4 mmol).

Synthesis of NPCNs-polymer and NPCNs-Co

NPCNs (10 mg) dispersed in 20 mL of ethanol solution, the 4,4'-Dihydroxy-3,3'diformylbiphenyl (2.5 mg, 0.01 mmol) were dissolved with ethanol/DMSO (2 mL, 10/1, v/v) was added into the above solution, and then 2,2-dimethyl-1,3-propanediamine (1 μ L, 0.01 mmol) was added dropwise into the solution. The resulting mixture was stirred at 70 ° C for 10 h. After the reaction, the solid was separated and washed with ethanol to remove the unresponsive ligand to obtain NPCNs-polymer, and then the solid was ultrasonically dispersed in 50 mL of ethanol solution, then Co(NO₃)₂·6H₂O (145.52 mg, 0.5 mmol) was added to the solution. After refluxed for 10 h, the solid was separated and washed with a large amount of ethanol to remove free metal ions. The filtered solid was vacuum dried to obtain NPCNs-Co.

Synthesis of Pt-NPs@NPCNs-Co and Pt-NPs@NPCNs

NPCNs-Co (10 mg) and (DMSO)Pt(Cl)₂ (2.5 mg) were ultrasonically dispersed in 20 mL of ethanol solution and refluxed for 10 h, the solid was separated by centrifugation, then washed with a large amount of ethanol and dried in an oven at 60 °C under vacuum overnight to obtain Pt-NPs@NPCNs-Co.

The Pt-NPs@NPCNs was synthesized by a similar procedure as that used for Pt-NPs@NPCNs-Co, except that NPCNS-Co is replaced by NPCNs-polymer.

Material characterization

The X-ray diffraction patterns (XRD) measurements were characterized by a SmartLab9KW diffractometer (Rigaku, Japan) with Cu K α radiation (λ =1.54178 Å) at room temperature. X-ray photoelectron spectroscopy (XPS) data was done on Thermo Scientific spectrometer. Fourier transform infrared (FT–IR) spectra were characterized by PerkinElmer Frontier Mid-IR FT-IR spectrometer using KBr pellets. Transmission electron microscopy (TEM) measurements were tested on a FEI Tecnai G2 Spirit TWIN at an acceleration voltage of 120 kV. The high resolution transmission electron microscopy (HRTEM) and EDS mapping were performed with a JEM-2100F microscope at an accelerating voltage of 200 kV. The contents of Co and Pt species in the samples were determined by inductively coupled plasma mass spectrometer (ICP-MS, iCAP RQ, Germany).

Electrochemical measurements

The electrocatalytic HER performance evaluation of catalysts was carried out in a CHI 760E electrochemical work-station using the standard three electrode setup at room temperature. The catalysts were loaded on a glass carbon electrode (3 mm in diameter) serving as the working electrode, a graphite rod and Ag/AgCl (sat. KCl) acting as the reference electrode and counter electrode. The electrocatalytic measurements were performed in an N₂ saturated aqueous solution of KOH (1 mol L⁻¹). The measured potential was calibrated to the reversible hydrogen electrode (RHE) using the following equation of $E_{(RHE)} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.198$.

Linear sweep voltammetry (LSV) curves were tested at a scan rate of 10 mV s⁻¹ in the potential range of 0 to - 0.7 V (vs. RHE) to evaluate the HER performance of catalysts. The ECSA of the catalyst was tested as the double layer capacitance (C_{dl}) by using cyclic voltammetry in the potential window of 0.1~0.2 V (vs. RHE) at the scan rates of 20, 40, 60, 80 and 100 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was carried out at a potential of -0.376 V from 0.1 to 10⁶ Hz by applying AC voltage of 5 mV.

The catalysts were prepared by adding 2 mg catalyst in Nafion/ethanol solution (5 wt%) to obtain 2.0 mg mL⁻¹ ink. The mixed suspensions were ultrasonicated for 60 min to form a

homogeneous solution. Then, 2 μ L portion of the resulting solution dispersion was uniformly dispersed on the polished glass carbon electrode before being dried at room temperature.

DFT calculations:

Spin-polarized density functional theory (DFT) calculations were performed with the Vienna Ab Initio Simulation Package (VASP).^{1.2} The Perdew-Burke-Ernzerhof (PBE) functional was taken into account the exchange and correlation effects.³ And the electron–ion interaction was described by the projected augmented wave (PAW) method.⁴ A cutoff energy of 400 eV was used for the planewave basis. The Gaussian smearing method with a smearing width of 0.05 eV was employed to determine partial occupancies. The van der Waals interactions was considered via DFT-D3 method.⁵ To balance the computational cost and accuracy, the convergence tolerance was set to 10⁻⁵ eV for energy variation and 0.03 eV/Å for force on each atom during the structure optimization. During the calculations, periodic boundary conditions were applied and a 15 Å vacuum layer was set to the (010) and (100) facets. And the Brillouin zone was sampled by a Monkhorst–Pack mesh with a 3 × 3 × 1 grid in reciprocal space. Structure optimization was finished until the residual Hellmann-Feynman forces were smaller than 0.02 eV/Å. Here, we considered three computational models for. The Gibbs free energies at 298.15 K and 1 atm were calculated with

$$G = E_{DFT} + E_{ZPE} + \int C_V dT - TS$$
(1)

where E_{DFT} is the electronic energy which is obtained directly from the DFT optimizations, E_{ZPE} is the zero-point vibrational energy, $\int C_V dT$ is the heat capacity, T is the temperature (298.15 K here), and S is the entropy.



Fig. S1. TEM image of NPCNs-Co.



Fig. S2. HRTEM image of Pt-NPs@NPCNs.



Fig. S3. HRTEM image and the corresponding EDS elemental mapping images of Co, Pt and P in Pt-NPs@NPCNs-Co.

| Sample | ICP-MS (Co wt %) | ICP-MS (Pt wt %) |
|-----------------|------------------|------------------|
| Pt-NPs@NPCNs-Co | 0.57 | 3.25 |
| Pt-NPs@NPCNs | / | 4.23 |
| NPCNs-Co | 4.73 | / |

Table S1. The contents of Pt and Co in the samples were determined by ICP-MS.



Fig. S4. High-resolution XPS spectra of (a) Full XPS spectrum, (b) N 1s, (c) O 1s of Pt-NPs@NPCNs-Co.



Fig. S5. High-resolution XPS spectra of (a) Full XPS spectrum, (b) N 1s, (c) O 1s of NPCNs-Co.



Fig. S6. High-resolution XPS spectra of (a) Full XPS spectrum, (b) N 1s, (c) O 1s of Pt-NPs@NPCNs.



Fig. S7. The TGA curve of the Pt-NPs@NPCNs-Co (red), Pt-NPs@NPCNs (blue), and NPCNs-Co (green). When the temperature reached 200°C, the mass loss of Pt-NPs@NPCNs-Co, Pt-NPs@NPCNs, and NPCNs-Co were 7.93%, 2.3%, and 1.97%, respectively.



Fig. S8. N₂ sorption isotherms at 77 K and pore size distribution of (a, b) Pt-NPs@NPCNs-Co and (c, d) Pt-NPs@NPCNs.



Fig. S9. Cyclic voltammeter measured from 20 to 100 mV s⁻¹ under alkaline medium and the corresponding Δj vs. scan rates plots.

| Catalysts | Rs (ohm) | Rct (ohm) |
|-----------------|----------|-----------|
| 20% Pt/C | 16.93 | 101.6 |
| Pt-NPs@NPCNs-Co | 12.97 | 172.5 |
| Pt-NPs@NPCNs | 15.00 | 250.6 |
| NPCNs-Co | 13.24 | 11681 |

Table S2. The Rs and Rct values in the samples.



Fig. S10. The polarization curves measured in 1 M KOH before and after 3000 CV cycles of Pt-NPs@NPCNs-Co.



Fig. S11. FT-IR and XRD of Pt-NPs@NPCNs-Co before and after the HER test.

| Sample | ICP-MS (Co wt %) | ICP-MS (Pt wt %) |
|----------------------------|------------------|------------------|
| eletrolyte | / | / |
| Pt-NPs@NPCNs of before HER | 0.57 ± 0.06 | 3.25 ± 0.15 |
| Pt-NPs@NPCNs of after HER | 0.55 ± 0.06 | 3.40 ± 0.15 |

 Table S3. The ICP-MS value of Pt-NPs@NPCNs-Co before and after the HER test.



Fig. S12. Atomic structural models of Pt (111).



Fig. S13. The illustration of the topological structure of Pt(111)-Co.

Reference

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